[Review Paper]

Development of Organosilica Membranes with Ionic Liquid-like Properties and Application to Organic Vapor Separation

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This review discusses the permeation and separation characteristics, the microstructure and the permeation mechanisms of organosilica membranes with ionic liquid (IL)-like properties, prepared from silylated ILs. The permeation and separation characteristics for binary toluene/H₂ mixture, methanol synthesis gas/vapor mixtures, binary toluene/CH₄ mixture and binary methanol/CH₄ mixture were studied. The membranes showed selective permeation of toluene and methanol against H₂, CO₂ and CH₄ at temperatures over 100 °C. The permselectivities were strongly controlled by the affinity of the permeated molecules for the ILs. The results showed that silylated IL-derived organosilica membranes show potential for selective recovery of organic vapors from inorganic/organic gases. Attenuated total reflectance infrared spectroscopy, N₂ adsorption, gas/vapor permeation tests and nanoporimetry were also performed to evaluate the microstructure and permeation mechanisms of the new concept of organosilica membranes. The membrane depended on two permeation pathways, “only the dense IL regions” and “organosilica network-derived micropores + dense IL regions.” Furthermore, the contributions of two permeation pathways to gas permeation were successfully evaluated based on the nanoporimetry characteristics.

Keywords

Organosilica membrane, Ionic liquid, Organic vapor separation, Permeation mechanism

1. Introduction

Ionic liquids (ILs) are a class of molten salts with melting points below 100 °C, and generally consist of organic cations and organic/inorganic anions. The cations are mainly, but not limited to, alkylated imidazole, pyrrole or pyridine derivatives, quaternized alkyl amines and alkyl phosphines, *etc.* Typical anions of ILs are halides, alkyl sulfates, fluorinated hydrocarbons, carboxylic acids and amino acids. ILs have superior physical and chemical properties, such as negligible vapor pressure, thermal stability and ability to dissolve CO₂ and a large range of organic molecules^{1,2)}, so have been widely studied in membrane separation processes for various gases and vapors such as CO₂^{3)~11)}, alkenes^{12)~18)} and aromatic hydrocarbons^{19)~23)}. The impregnation method is widely used for membrane synthesis due to the simple preparation procedure, but “blow-out” of ILs from the porous support under high cross-membrane pressure differences is the main disadvantage of supported IL membranes (SILMs). The effects of the membrane structure and cross-membrane pressure difference on membrane liquid loss behaviors

of SILMs have been investigated²⁴⁾. Blow-out of ILs depends on the materials and structure of the support membranes, but SILMs are stable under cross-membrane pressure of 0.3 MPa. However, IL membranes are also expected to resist extreme conditions such as high pressure conditions and coexistence of steam and organic vapors.

Several membrane preparation methods have been investigated for the synthesis of highly stable IL membranes, including polymerization^{4),25)~27)}, gelation^{9)~11),28)} and chemical stabilization methods^{29)~31)}. Chemically stabilized IL membranes were developed by grafting silylated ILs onto the pore surface of ceramic nanofiltration membranes, and evaluation of CO₂/CO separation performances found a maximum separation factor of 25 at 60 °C²⁹⁾. However, the pores are difficult to fully fill with silylated ILs by the stabilization method. Thus, separation performances were not always equal to those of SILMs due to the presence of voids. Consequently, further optimization was required to fill the pores with silylated ILs to improve the separation performance.

The author and co-workers have developed organosilica membranes with IL-like properties on nanoporous ceramic tubes using silylated ILs as precursor chemicals^{32)~34)}. In contrast to the previous stabilization

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Compounds SipmimCl and SipbenzylimCl are hydrophilic ILs, and SipmimTf₂N and SipbenzylimTf₂N are hydrophobic ILs.

Fig. 1 Representation of the ILs Used in This Study

method^{29,30}), polycondensed silylated ILs were introduced into the pores of substrates to form a composition. The silylated IL-derived organosilica membranes showed superior permselectivity for organic vapors against inorganic/organic gases with superior durability compared to SILMs.

This review describes the permeation and separation characteristics, the microstructure and the permeation mechanisms of our new concept for organosilica membranes, and demonstrates the permselectivity for methanol against CH₄.

2. Preparation of Silylated ILs and Membranes

Four types of silylated IL were synthesized and used as precursor chemicals with molecular structures as summarized in **Fig. 1**. Preparation procedures for these silylated ILs are described elsewhere^{32)~34)}. The SipmimTf₂N, SipmimCl and SipbenzylimTf₂N-derived organosilica membranes were formed on nanoporous ceramic tubes by a solvent-free solvothermal method³²⁾, a hot-dip coating method³³⁾, and a sol-gel method³⁴⁾, respectively.

The hydrophilic SipbenzylimCl-derived organosilica membrane was also prepared on a nanoporous alumina tube by a sol-gel method. Firstly, a nanoporous alumina layer was formed on α -alumina porous tube (purchased from Noritake Co., Ltd.) with length of 30 mm, diameter of 10 mm, thickness of 1 mm and pore size of 150 nm. The tube was coated twice with boehmite/polyvinyl alcohol sol, and calcined at 500 °C, resulting in the γ -alumina layer with pore diameter of 7 nm. The boehmite solution was supplied by Kawaken Fine Chemicals Co., Ltd. The pore size of the nanoporous alumina layer was determined by a nanoporimetry method. A mixture of synthesized SipbenzylimCl (0.05 mol) and 3.75 mL of NH₃ aqueous solution (1 mol/L, Kanto Chemical Co., Inc.) was stirred at 20 °C for 24 h, to obtain SipbenzylimCl-derived sol. The organosilica membrane was prepared by dip-coating of the sol on the alumina tube, followed by heating at

250 °C for 3 h.

3. Permeation and Separation Characteristics of Silylated IL-derived Organosilica Membranes

3.1. Permeation and Separation of Toluene/H₂ Mixture

Organic chemical hydrides, which are hydrogenated aromatic hydrocarbons (*e.g.*, methylcyclohexane), offer many advantages, such as high H₂ content and ease of transportation³⁵⁾. In manufacture, the technology of H₂ separation and purification from organic molecules is one of the key issues. We previously applied IL membranes to the organic chemical hydride process as an innovative technology for H₂ purification by removing hydrocarbons from the mixture^{32),36)}.

Permeation and separation characteristics of the hydrophobic SipmimTf₂N-derived organosilica membrane were studied in a binary toluene/H₂ mixture system. For comparison, SILM was also prepared by impregnating the same substrate with as-made SipmimTf₂N. To evaluate the durability, the membrane after the permeation test was dried under vacuum to remove absorbed toluene, and the amount of blow-out of IL was calculated by measuring the weight change before and after the permeation test.

Figure 2 shows the time courses of toluene and H₂ permeance and separation factors through the membranes. The separation test was conducted at 70 °C using partial pressures of toluene and H₂ of 30 kPa and 90 kPa, respectively. The H₂ permeances at 0 min were obtained from a single H₂ permeation test. The conditions of the single H₂ permeation test were the same as those of the toluene/H₂ separation test, except for the feed component. Both membranes showed selective permeation of toluene against H₂. The maximum toluene/H₂ separation factor of the SipmimTf₂N-derived organosilica membrane was over 17,000 after 180 min. The toluene and H₂ permeances were 2.3×10^{-7} mol m⁻² s⁻¹ Pa⁻¹ and 1.3×10^{-11} mol m⁻² s⁻¹ Pa⁻¹, respectively. Separation performance of the organosilica membrane was superior to that of the SipmimTf₂N-impregnated membrane (selectivity of 1280 for toluene against H₂ after 90 min). Permeation through liquid membranes, including SILMs, is normally explained by the solution-diffusion mechanism. According to this mechanism, membrane selectivity is influenced by the membrane's affinity for the feed molecules and the ease of diffusion of molecules through the membrane. Hydrogen is significantly less soluble in ILs compared with H₂O, alcohol and hydrocarbons²⁾. The results of the permeation tests indicate that the permselectivity of the SipmimTf₂N-derived organosilica membrane is strongly controlled by the affinity of toluene toward the IL, for the impregnated membrane.

The H₂ permeance of the SipmimTf₂N-impregnated

Permeation temperature is 70 °C. Partial pressures of toluene and H₂ in the feed stream are 30 kPa and 90 kPa, respectively.

Fig. 2 Time Courses of Toluene and H₂ Permeances and Separation Factors for (a) the SipmimTf₂N-derived Organosilica and (b) the SipmimTf₂N-impregnated Membranes

membrane in the binary mixture permeation test increased with permeation time. We also observed that the IL content in the tube after 180 min decreased by 30 % compared to that before the permeation tests. This blow-out of IL would affect the H₂ diffusivity in the impregnated membrane, resulting in higher H₂ permeance. In contrast, the H₂ permeance of the SipmimTf₂N-derived organosilica membrane did not change significantly after the addition of toluene in the feed stream. Compared to the impregnated membrane, the amount of blow-out of IL from the tube was reduced to 3 % after 180 min.

The silylated IL-derived organosilica membrane showed excellent potential for H₂ purification in the organic chemical hydride process by removing aromatic hydrocarbon from the binary system with superior durability compared to SILMs.

3.2. Permeation and Separation of Methanol Synthesis Gas/Vapor Mixtures

The thermodynamic equilibrium in methanol synthesis results in low conversion per pass, and methanol synthesis is usually performed at pressures of 5–10 MPa and temperature of about 250 °C. The membrane reactor could be used to improve the conversion per pass of methanol synthesis³⁷⁾. The yield of methanol was increased by continuous removal of methanol and H₂O from the reactor through Nafion membranes. The permselectivities of Nafion, silicon rubber/ceramic composite³⁸⁾ and zeolite membranes^{39)–45)} for methanol have been investigated. However, simultaneous separation of methanol and H₂O from H₂ at high temperature is still difficult, so further development of separation membranes is needed. We investigated the use of IL membranes for separation of the methanol synthesis gas/vapor mixtures³³⁾.

The hydrophilic SipmimCl-derived organosilica membrane was evaluated for the separation of methanol synthesis gas/vapor mixtures. The temperature depen-

Partial pressures of methanol and H₂ in the feed stream are 15 kPa and 85 kPa, respectively.

Fig. 3 Temperature Dependence of Permselectivity of the SipmimCl-derived Organosilica Membrane in a Methanol/H₂ Binary Mixture System

dence of methanol and H₂ permeances in the binary mixture system are shown in **Fig. 3**. Partial pressures of methanol and H₂ in the feed stream were 15 kPa and 85 kPa, respectively. Although the separation performance of the SipmimCl-derived organosilica membrane decreased with higher permeation temperature, separation factors of more than 10 were still obtained at 200 °C. The activation energies of permeation (E_p) through the organosilica membrane were calculated using the Arrhenius equation, and values of 2.8 kJ mol⁻¹ for methanol and 23 kJ mol⁻¹ for H₂ were obtained. The obtained E_p of H₂ was much larger than those of other amorphous silica and organosilica membranes^{46)–48)}. The IL groups in the membrane affected the H₂ permeation at temperatures up to 200 °C.

Table 1 Comparison of Permselectivity of the SipmimCl-derived Organosilica Membrane in the Binary and Quaternary Mixture Systems

Feed stream	Permeance [$10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$]				Separation factor [-]			
	Methanol	H ₂	CO ₂	H ₂ O	Methanol/H ₂	Methanol/CO ₂	H ₂ O/H ₂	H ₂ O/CO ₂
Methanol/H ₂	11	0.94	-	-	12	-	-	-
Methanol/H ₂ O/H ₂ /CO ₂	11	1.1	4.1	30	10	26	29	74

Permeation tests were conducted at temperature of 200 °C and total pressure of 101 kPa. Molar compositions of the feed stream are methanol : H₂ = 15 : 86 for the binary system, and methanol : H₂O : H₂ : CO₂ = 15 : 4 : 72 : 10 for the quaternary system.

Table 2 Comparison of Separation Performance of the SipmimCl-derived Organosilica Membrane at 200 °C with the Data Previously Reported

Membrane	Feed stream	Permeance [$10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$]		Separation factor [-]		Ref.
		CH ₃ OH	H ₂ O	CH ₃ OH/H ₂	H ₂ O/H ₂	
Li-Nafion	ternary	0.3	5.0	5.6	32	37)
Mordenite	ternary	< 0.01	7.1	< 0.1	78	42)
Na-ZSM-5	binary	19	28	117	22	43)
SipmimCl	quaternary	11	30	10	29	Our work 33)

Permeation tests were conducted in binary mixtures of methanol/H₂ or H₂O/H₂, ternary mixtures of methanol/H₂O/H₂, methanol/H₂/CO₂ or H₂O/H₂/CO₂, and a quaternary mixture of methanol/H₂O/H₂/CO₂. Total pressure of the feed side was atmospheric pressure, and partial pressures of methanol and H₂O were < 20 kPa and < 10 kPa, respectively. All permeation tests were performed in the temperature range from 200 to 250 °C.

Table 1 shows the permselectivity of the SipmimCl-derived organosilica membrane at 200 °C in the binary and quaternary mixture systems. The membrane also showed high H₂O/H₂ and H₂O/CO₂ separation performances in the quaternary system. Methanol permeation was not affected by the presence of H₂O and CO₂ in the feed stream. The separation performance is compared with those of other membranes in **Table 2**. Methanol and H₂O permeances of the SipmimCl-derived organosilica membrane were higher than those of the Li-Nafion membrane, and comparable to those of the Na-ZSM-5 membrane. **Figure 4** shows the pressure dependence of permeation characteristics in the quaternary mixture system. The membrane could separate methanol and H₂O from H₂ and CO₂ under feed pressures up to 0.3 MPa.

The silylated IL-derived organosilica membrane demonstrated excellent potential for the simultaneous separation of methanol and H₂O from H₂ and CO₂ at high temperature.

3.3. Permeation and Separation of Toluene/CH₄ and Methanol/CH₄

Conversion of CH₄ to valuable chemicals such as aromatic hydrocarbons and methanol is commercially attractive because of the vast abundance and low cost of natural gas. Nonoxidative CH₄ aromatization to produce benzene over Mo loaded zeolite catalysts has been widely studied⁴⁹⁾. The main challenges in this reaction process are the thermodynamic limitations that constrain CH₄ conversion at low temperature and the inherent coke deposition over the active sites of the catalysts leading to fast deactivation. A direct methane oxidation pathway to methanol at low temperature would be effective compared to the present processes. Copper-loaded zeolites and metal-organic-frameworks are

Molar composition of the feed stream is methanol : H₂O : H₂ : CO₂ = 15 : 4 : 72 : 10.

Fig. 4 Effect of Feed Side Total Pressure on Permselectivity of the SipmimCl-derived Organosilica Membrane in the Methanol/H₂O/H₂/CO₂ Quaternary Mixture System

active and selective for CH₄ oxidation at moderate temperatures^{50)~52)}, but the yield is still low. Further development is required for the industrial adoption of direct CH₄-to-chemicals processes. We have focused on the development of aromatics and methanol-selective membranes. Removal of aromatics and methanol from the reactor through such membranes may prevent further reactions of aromatics and methanol, leading to improvement in both yields and catalyst lifetime. However, membrane separation of aromatic hydrocarbons/CH₄ and methanol/CH₄ has not been reported. We applied our innovative IL membranes to those sepa-

Partial pressures of toluene and CH₄ in the feed stream are 3.4 kPa and 97.6 kPa, respectively.

Fig. 5 Temperature Dependence of Permselectivity of the SipbenzylimTf₂N-derived Organosilica Membrane in a Toluene/CH₄ Binary Mixture System

ration systems.

The hydrophobic SipbenzylimTf₂N-derived organosilica membrane was studied for the separation of a binary toluene/CH₄ mixture³⁴. The temperature dependence of the permselectivity of the membrane in the toluene/CH₄ binary mixture system is shown in Fig. 5. The partial pressure of toluene in the feed stream was 3.4 kPa in these tests. The maximum toluene/CH₄ separation factor of 13 was obtained at 50 °C. The toluene and CH₄ permeances were $8.7 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and $6.6 \times 10^{-11} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively. Both permeances increased with higher temperature, but CH₄ permeance increased faster than toluene permeance. As a result, the separation performance of the SipbenzylimTf₂N-derived organosilica membrane decreased with higher temperature. However, the membrane still showed selectivity of 4.8 for toluene against CH₄ at temperatures up to 170 °C.

Permeation and separation characteristics of the hydrophilic SipbenzylimCl-derived organosilica membrane were studied in a binary methanol/CH₄ mixture system. The separation test apparatus and method were same as those of the toluene/CH₄ separation test³⁴, except for the vapor component. Temperature dependence of the permselectivity of the membrane is shown in Fig. 6. The partial pressures of methanol and CH₄ in the feed stream were 15 kPa and 86 kPa, respectively. Separation performance of the membrane decreased with higher permeation temperature, but separation factor of more than 40 was still obtained at 200 °C. Figure 7 shows the effect of CH₄ partial pressure in the feed stream on the permselectivity of the membrane. The permeation temperature was 100 °C,

Partial pressures of methanol and CH₄ in the feed stream are 15 kPa and 86 kPa, respectively.

Fig. 6 Temperature Dependence of Permselectivity through the SipbenzylimCl-derived Organosilica Membrane in a Methanol/CH₄ Binary Mixture System

Total pressure of the feed stream was 101 kPa, and permeation temperature was 100 °C.

Fig. 7 Effect of Methanol Concentration in the Feed Stream

with the feed side pressure maintained at atmospheric pressure. The maximum methanol/CH₄ separation factor of 278 was obtained at methanol partial pressure of 5.2 kPa. The methanol and CH₄ permeances were $1.0 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and $3.6 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, respectively. The SipbenzylimCl-derived organosilica membrane could recover methanol from the binary mixture at low concentrations of methanol in the feed streams.

These investigations of the application of IL-based membranes for separation of aromatics/CH₄ and methanol/CH₄ found that silylated IL-derived organosilica

Fig. 8 ATR-IR Spectra of (a) As-made SipmimCl and (b) SipmimCl-derived Organosilica Gel after Thermal Treatment at 200 °C

membranes show potential for selective recovery of aromatic hydrocarbons and methanol in direct CH₄-to-chemicals reactions.

4. Microstructure and Permeation Mechanism of Silylated IL-derived Organosilica Membranes

The silylated IL-derived organosilica membranes showed superior selective permeation of organic vapors and H₂O against inorganic/organic gases with improved durability than the SILM. Permselectivity of the organosilica membranes was strongly controlled by the affinity of the permeate molecules toward the ILs. For further applications, the microstructure and the permeation mechanisms of this new concept of organosilica membranes should be discussed. We evaluated the microstructure of the SipmimCl-derived organosilica gel and membrane by attenuated total reflectance infrared spectroscopy (ATR-IR), N₂ adsorption measurement and gas/vapor permeation tests³³. Nanopermporometry was also performed on the SipbenzylimTf₂N-derived organosilica membrane for further characterization of the permeation mechanism³⁴.

4.1. Microstructure

Figure 8 shows the ATR-IR spectra of as-made SipmimCl and IL after hydrolysis and thermal treatment at 200 °C. Thermal treated samples were prepared on the Si substrate, and the resultant materials on the substrate were moved to the diamond crystal. Peaks at 960 cm⁻¹ and 1080 cm⁻¹ are assigned to the ethoxy group⁵³, and their peak intensities decreased after these treatments. The peak of the Si-O-Si band (spectral range of 1200-1000 cm⁻¹)⁵³ appeared after the treatments, indicating that SipmimCl molecules were well hydrolyzed, and the organosilica network was formed *via* cross-linking of the hydrolyzed IL molecules.

Permeances of gases and vapors through the SipmimCl-derived organosilica membrane at 20 °C are shown in Fig. 9. The permeances of H₂O and metha-

Total feed side pressures in the single gas system and the gas/vapor mixture system are 121 kPa and 101 kPa, respectively. Partial pressures of H₂O and methanol are 2.1 kPa and 12.5 kPa.

○: single gas system, △: H₂O/H₂ binary system, ◆: CH₃OH/H₂ binary system.

Fig. 9 Permeances of Gases and Vapors through the SipmimCl-derived Organosilica Membrane at 20 °C

nol were higher than those of gases, regardless of their kinetic diameters. H₂ permeance values were smaller for the binary mixture permeation tests than for the single H₂ permeation (1.8×10^{-9} mol m⁻² s⁻¹ Pa⁻¹). Porous membranes such as zeolite, silica and carbon membranes have been developed as molecular sieve-based membranes which allow small molecules to selectively permeate. On the other hand, such membranes also show reverse-selectivity, in which larger molecules selectively permeate through the membranes. Hydrogen permeation through zeolite membranes was decreased in the presence of H₂O and/or methanol. Preferential adsorption of methanol in the micropores of zeolite hindered the permeation pathways of H₂^{39),40),43}. Consequently, these zeolite membranes showed reverse-selectivity. Similar permeation and separation properties have been reported for silica membranes⁵⁴. The permeation characteristics of the SipmimCl-derived organosilica membrane indicate that the silylated IL-derived organosilica membrane contained few micropores, but preferential adsorption of H₂O and methanol in these pores hindered H₂ permeation.

N₂ adsorption measurements were also performed to investigate the microstructure of the SipmimCl-derived organosilica membrane. We measured N₂ adsorption isotherms of the SipmimCl-derived organosilica gel after thermal treatment at 200 °C and SipmimCl-derived silica powder obtained by removing the IL group through calcination treatment at 500 °C under O₂ flow. The SipmimCl-derived gel did not adsorb N₂ molecules, but the SipmimCl-derived silica powder did adsorb N₂ molecules (Fig. 10). Pore size distribution was calcu-

Fig. 10 N₂ Adsorption Isotherms of the SipmimCl-derived Organosilica Gel and Silica Powder

lated from the isotherms by the SF method, indicating that the silica powder had 0.6 nm-sized micropores. The pore size distribution of the membrane was not equal to that of the SipmimCl-derived silica powder because of the difference in thermal treatment temperature. Considering the effect of thermal contraction through calcination at 500 °C, the SipmimCl-derived organosilica membrane would have micropores with pore sizes larger than 0.6 nm.

These results indicate that silylated IL-derived organosilica membranes, including the SipmimCl-derived membrane, contain micropores like many other molecular sieving-organosilica membranes. However, the micropores were covered and/or occupied by the branched IL. The outer surface of the membrane is covered with the IL, which results in the SILM-like properties.

4.2. Permeation Mechanism

The results of the ATR-IR, N₂ adsorption measurement, and gas/vapor permeation tests indicated that silylated IL-derived organosilica membranes incorporate two types of permeation pathways; gas and vapor molecules diffuse through (1) only the dense IL regions and (2) both the micropores and the dense IL regions. The former pathway involves the solution-diffusion mechanism as well as the SILMs. The latter permeation pathway is similar to that of porous membranes, including surface diffusion flow and Knudsen diffusion flow.

Nanopermporometry is an effective method to evaluate active pores, which contribute to the permeability of porous membranes^{55),56)}. We performed nanopermporometry on the SipbenzylimTf₂N-derived organosilica membrane for further characterization of the permeation mechanism³⁴⁾. The H₂ permeance was monitored in the presence of capillary condensation of *n*-hexane vapor. **Figure 11** shows the dimensionless

Fig. 11 Dimensionless Permeance of H₂ Measured by Nanopermporometry with *n*-Hexane as a Condensable Vapor

permeance of H₂ as a function of the Kelvin diameter. The H₂ permeance sharply decreased with Kelvin diameter of less than 1 nm, suggesting that SipbenzylimTf₂N-derived organosilica membrane contained about 1 nm-sized micropores. Although the H₂ permeance decreased with higher Kelvin diameter, the value did not become unmeasurable with Kelvin diameter of about 24 nm. About 22 % of H₂ permeance ($= 3.3 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) was still observed. The organosilica membrane was prepared on the nanoporous alumina layer, with pore size of 7 nm. Therefore, the SipbenzylimTf₂N-derived organosilica membrane would not contain 24 nm-sized pores. As mentioned above, we concluded that the organosilica membrane allows gas and vapor molecules diffuse through (1) only the dense IL regions and (2) both the micropores and the dense IL regions. The latter permeation pathway would be blocked by condensation of *n*-hexane in the pores. Therefore, we considered that 78 % of H₂ molecules would permeate through pathway-2 (both micropores and dense IL regions), and the remaining 22 % of H₂ molecules would permeate through pathway-1 (only dense IL regions) by the solution-diffusion mechanism.

To assess the adequacy of the estimated H₂ permeance, H₂ permeability through the SipbenzylimTf₂N-derived organosilica membrane was compared with that for a SILM prepared by the impregnation method using IL, 1-benzyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (benzylmimTf₂N, io-li-tec, > 98 %). A polyvinylidene difluoride (PVDF) membrane with mean pore size of 0.2 μm and typical thickness of 127 μm (Pall, FluoroTrans® PVDF membrane) was employed as the support. Due to its similar molecular structure with SipbenzylimTf₂N, benzylmimTf₂N was selected for comparison. The benzylmimTf₂N/PVDF membrane was a typical SILM and H₂ permeation through the membrane depends on the solution-

Table 3 Comparison of H₂ Permeability for the SipbenzylimTf₂N Membrane (part of the solution and diffusion mechanism) and the BenzylimTf₂N Membrane

Membrane	Membrane thickness [μm]	H ₂ permeability [$10^{-15} \text{ mol m m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$]
SipbenzylimTf ₂ N-derived organosilica	5	1.6
BenzylimTf ₂ N/PVDF	127	3.2

diffusion mechanism. Membrane thicknesses and H₂ permeabilities of both membranes are summarized in **Table 3**. The values of the estimated H₂ permeability of the organosilica membrane through permeation pathway-2 was of the same order as that of the SILM, indicating that 22 % of H₂ molecules permeated through the dense IL regions in the SipbenzylimTf₂N-derived organosilica membrane through the solution-diffusion mechanism.

Therefore, nanoporometry could successfully evaluate the micropore size in the silylated IL-derived organosilica membrane, and the contributions of the two permeation pathways to the overall gas permeation.

5. Conclusion

Silylated IL-derived organosilica membranes were fabricated on nanoporous ceramic tubes, and the permeation and separation properties for binary toluene/H₂ mixture, methanol synthesis gas/vapor mixtures, binary toluene/CH₄ mixture and binary methanol/CH₄ mixture were studied at high temperatures up to 200 °C. The membranes showed selective permeation of toluene and methanol against H₂, CO₂ and CH₄. Therefore, silylated IL-derived organosilica membranes show potential for selective recovery of organic vapors from inorganic/organic gases.

The separation tests also revealed that the permselectivities were strongly controlled by the affinity of the permeated molecules for the ILs, and the permeation and separation mechanisms were a combination of the selective adsorption/pore blocking effect and the solution-diffusion mechanism. N₂ adsorption measurements suggested that the silylated IL-derived organosilica membranes contained micropores derived from the organosilica network, but the micropores were covered and/or occupied by the branched IL. The membrane depended on two permeation pathways, “only the dense IL regions” and “organosilica network-derived micropores + dense IL regions.” The suggested microstructure of the organosilica membranes can explain the permeation and separation properties. Furthermore, nanoporometry characterization of the SipbenzylimTf₂N-derived organosilica membrane successfully evaluated the contribution of the two permeation pathways to the overall gas permeation. The results indicated that about 80 % of H₂ molecules permeated through “both dense IL regions and micropores,” and the remaining 20 % molecules permeated through “only

dense IL regions” through the solution-diffusion mechanism.

The affinity of ILs for chemicals can be controlled by the combination of cation and anion. Silylated IL-derived organosilica membranes can be designed by using various IL structures to provide feasible and desirable separation performances for various systems. Findings of detailed microstructure and permeation mechanism will be also useful for the future design of silylated-IL derived organosilica membranes.

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Abbreviations

Sipmim = 1-methyl-3-(1-triethoxysilylpropyl)imidazolium

Sipbenzylim = 1-benzyl-3-(1-triethoxysilylpropyl)imidazolium

Tf₂N = bis(trifluoromethylsulfonyl)imide

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要 旨

イオン液体の特性をもつオルガノシリカ膜の開発と有機蒸気分離への応用

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本総合論文では、シリル化イオン液体を膜素材としたイオン液体の特性をもつオルガノシリカ膜の透過分離特性、膜構造そして透過機構について紹介する。トルエン／水素、メタノール合成ガス・蒸気、トルエン／メタンおよびメタノール／メタン混合系でのシリル化イオン液体由来オルガノシリカ膜の透過分離能を評価した。作製した膜は100℃以上の温度域においても水素、二酸化炭素、メタンに対して、トルエンおよびメタノールの選択透過性を示した。膜の選択透過性はイオン液体への透過分子の親和性により発現していることを明らかにした。これらの結果から、シリル化イオン液体由来オルガノシリカ膜

は各種の無機・有機ガスから有機蒸気を選択的に回収する分離膜として有望な選択肢といえる。同時に、新規オルガノシリカ膜の構造と透過機構の解明を目的とし、全反射赤外分光測定、窒素吸着、ガス・蒸気透過試験およびナノパーンプポロメトリー評価を行った。これらの評価から、当該分離膜には「イオン液体密集部のみ」と「シリカネットワーク由来マイクロ孔＋イオン液体密集部」の二つの透過経路の存在が明らかとなった。さらに、ナノパーンプポロメトリー評価から、ガス透過における二つの透過経路の寄与率を算出することに成功した。

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